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Oxygen gettering by hafnium implanted in beryllium: A ⟨0001⟩ Hf-O dumbbell?

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The interaction of hafnium implanted into beryllium single crystals with diffusing oxygen was studied using hyperfine interaction and Rutherford backscattering channeling techniques. It was observed that oxygen is trapped at hafnium in a well defined lattice position. The formation of a ⟨0001⟩ Hf-O mixed dumbbell in the tetrahedral interstitial cage of the beryllium lattice is suggested to explain the experimental results.

Beryllium metal has been thoroughly studied in recent years since its elemental properties make it very important for nuclear technology.[1] One of the major problems hampering its more widespread technical application is its usually very low ductility thought to be due to impurities. All efforts to surpass this disadvantage by forming controlled alloys have been unsuccessful up to now. Systematic investigations of the influence of nonmetallic impurities like oxygen and carbon on the purification and alloying behavior of Be have been carried out; the results, however, were largely inconclusive.[2,3]

Recently the Rutherford backscattering (RBS) channeling technique has been applied to Be metal to systematically investigate the formation of substitutional and interstitial alloys with this metal and some rules concerning the formation of metastable alloys have been found.[4] In particular it was found that hafnium implanted in Be populates preferentially the tetrahedral interstitial site in the hcp Be lattice.[5] The thermal annealing behavior of this system was studied in RBS/channeling and time differential perturbed angular correlation (TDPAC) measurements in the temperature range up to 657 K.[6]

In the present work we studied the interaction of the implanted Hf with oxygen in the Be lattice. It is well known that atoms with a strong affinity to oxygen dissolved in small quantities in metals with a smaller affinity to oxygen may trap diffusing oxygen, a process usually called internal gettering. Hafnium like titanium and zirconium is known to be a very good gettering material.[7] Here we present a detailed study of the trapping process where the microscopic environment of the Hf probe atoms was studied by the TDPAC technique,[5,6] the nuclear orientation (NO) technique,[8] and the RBS/channeling technique.[4,5]

The Be single crystals used in this work were cut approximately perpendicular to the ⟨10$\bar{1}$0⟩ axis and electropolished before the implantation. Minimum RBS yields obtained for the ⟨11$\bar{2}$0⟩ axis lie typically between 10% and 20%. Three pieces cut from the same single crystal were used. The dilute HfBe alloys were prepared by implantation of 80-keV Hf ions with the Bonn electromagnetic separator. During implantation the crystals were kept at 293 K in a vacuum better than 10^{-5} mbar. The crystal surface was oriented perpendicular to the beam so that possible channeling of the Hf ions cannot be excluded. The crystal numbered I was implanted with 2.4×10^{12} at/cm^2 of radioactive ^{181}Hf and the crystal numbered II was implanted with 7×10^{14} at cm^2 of radioactive ^{175}Hf. The radioisotopes were produced by thermal neutron irradiation of natural HfO_2. Peak volume concentrations of 5 and 1400 at. ppm of Hf in Be crystals I and II were estimated. Crystal III was implanted with 4.2×10^{14} at/cm$_2$ of stable ^{179}Hf for a lattice location measurement of the Hf atoms.

After the implantation of crystal I a TDPAC measurement was carried out at 239 K using the 133–482-keV γ-γ cascade of ^{181}Ta populated in the decay of the implanted ^{181}Hf to observe the spin rotation of the 482-keV state of ^{181}Ta [Fig. 1(a)]. Subsequently the crystal was annealed isochronously (holding time = 30 min) in a vacuum of better than 10^{-6} mbar at several temperatures between 620 and 843 K. After each annealing step TDPAC spectra were taken, an example of which is given in Fig. 1(b).

From the amplitude of the undamped quadruple interaction (QI) pattern observed immediately after implantation, Fig. 1(a), one can conclude that about 95% of the Hf probe atoms have come to rest in a well defined environment in the Be lattice and that damage caused by the implantation process is negligible. The observed QI frequency of $\nu_Q = eQV_{zz}/h = 227.0\ (22)$ MHz, with Q the nuclear quadruple moment of the 482-keV state of ^{181}Ta and V_{zz} the principal component of the electric field gradient (EFG) at the site of the ^{181}Ta nucleus, agrees well with the results of previous measurements.[5,6]

Annealing at temperatures above 620 K apparently leads to a drastic change of the charge distribution around the Hf probe atoms as shown by the appearance of a new, much higher QI frequency [Fig. 1(b)]. The fraction of Hf atoms in this new configuration reaches a value of 75% after annealing at 843 K. A least squares fit to the data yields $\nu_Q = 1420\ (14)$ MHz for this new frequency. Using the known quadruple moment of the 482-keV state in ^{181}Ta of

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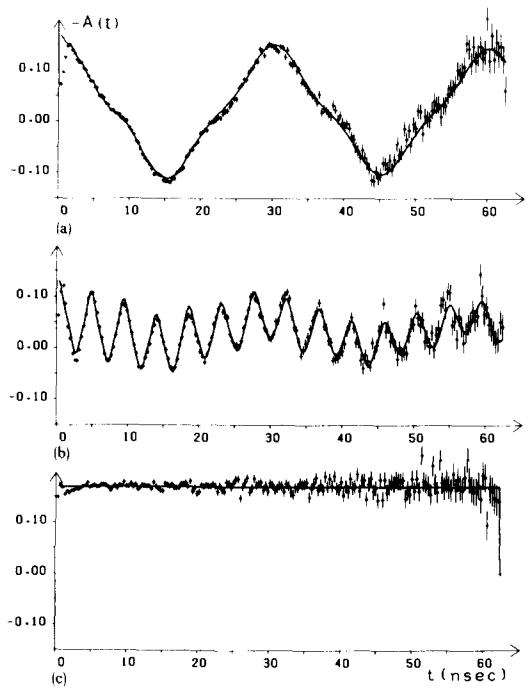

FIG. 1. Time dependent anisotropy A (t) of the 133–482-keV cascade for ^{181}Ta in beryllium single crystal: (a) as implanted, (b) after annealing at 843 K, (c) after annealing at 843 K but with the c axis in the direction of one γ detector.

$Q = +2.51(15)b$ [10] an EFG of $|V_{zz}| = 23.2\times10^{17}$ V/cm^2 is derived. In order to check if the new environment of the Hf probe atoms is still correlated to the lattice symmetry or possibly due to precipitation of Hf an additional measurement was carried out with the c axis of the Be crystal directed towards one of the γ detectors. In this geometry no perturbation of the angular correlation is expected, if the EFG at the site of Hf has axial symmetry with respect to the c axis.[11] Indeed no perturbation of the anisotropy was observed [Fig. 1(c)] and we can thus conclude that the new QI frequency is due to a change of the near surrounding of the Hf atom preserving axial symmetry with respect to the c axis.

The sign of the EFG at the site of the Hf probe, which cannot be inferred from the γ-γ TDPAC experiments, was determined by a NO experiment. To this purpose ^{175}Hf was implanted into crystal II and the anisotropy of the 343-keV γ line in the decay of ^{175}Hf was measured at very low temperatures where the population of the hyperfine split substates of the ground level of ^{175}Hf becomes unequal. To cool the sample a ^{3}He–^{4}He dilution refrigerator was used; details of the apparatus are described elsewhere.[8] Two measurements were performed, the first with the crystal as implanted, the second after the crystal had been subjected to the same annealing treatment up to 843 K as crystal I. For the QI frequency we deduce $\nu_Q = -163$ (20) MHz before annealing and $\nu_Q = -517$ (16) MHz after annealing. Inserting the quadruple moment of ^{175}Hf as $Q = +2.7$ (4) b [9] we derive $V_{zz} = -2.5\times10^{17}$ V/cm^2 and $V_{zz} = -7.8\times10^{17}$ V/cm^2, respectively. While the sign of these values can be derived free of systematic errors the absolute magnitude represents only a lower limit of the true EFG since Hf nuclei which after implantation come to rest in a nonunique environment do not contribute to the anisotropy and thus reduce

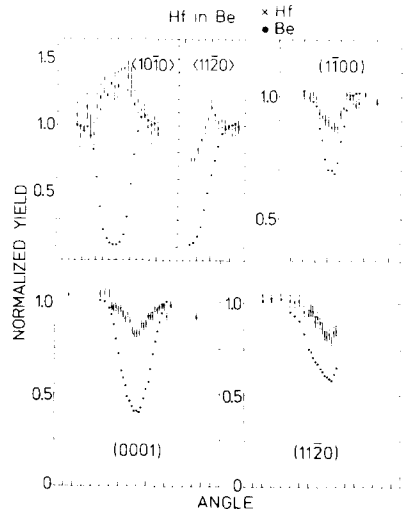

FIG. 2. Axial and planar scans for Hf implanted in Be after annealing at 843 K.

the value of ν_Q derived from the data. The high dose of Hf in crystal II may be one of the reasons for this effect. Comparison of the NO data for detection of the γ quanta at 0° and 90° against the c axis assures the EFG to be parallel to the c axis.

Parallel to this investigation RBS/channeling measurements were carried out with the 2-MV van de Graaff at Sacavém (Portugal). A 1.2-MeV He$^+$ beam collimated to $\pm$ 0.05° was used to scan the major symmetry axes of the Be crystals mounted in a two-axis goniometer.[12] For crystal III implanted with stable ^{180}Hf the angular scans taken after the implantation and before annealing confirmed the tetrahedral interstitial site of Hf in Be as observed by Kaufmann *et al.*[5]

The lattice location of Hf after the annealing process was determined using crystal II. Angular scans of the ⟨10$\bar{1}$0⟩ and ⟨11$\bar{2}$0⟩ axes and the (0001), (1$\bar{1}$00), and (11$\bar{2}$0) planar channels were performed and the results are shown in Fig. 2. Clearly the scans show that Hf did not precipitate but still occupies a nonsubstitutional site. The patterns are not typical for an impurity in either the ideal tetrahedral or octahedral interstitial site in the hcp Be lattice (see e.g., Ref. 5). However, since the ⟨11$\bar{2}$0⟩ as well as the (0001) and (1$\bar{1}$00) scans show a dip for the impurity, a position of Hf near the ideal octahedral site can be excluded. On the other hand, the data can be qualitatively explained with a position of Hf in the tetrahedral cage displaced from the ideal tetrahedral site in the c direction towards the center of the (0001) planar channel.

To further elucidate the mechanism producing the high EFG at the new site of the Hf probe atoms the RBS spectra of crystal II before and after annealing were analyzed. Special attention was given to possible changes in the carbon and oxygen depth profiles. It was observed that whereas the carbon peak did not change a broad oxygen peak appeared to the left of the always present surface oxygen peak. This indicates a concentration of oxygen in a layer well below the crystal surface. With the known stopping power of the 1.2-MeV He$^+$ particles in Be the depth distribution of oxygen could be calculated from the spectra and compared to that of the implanted Hf. As shown in Fig. 3 the two distributions overlap perfectly. We therefore conclude that the observed

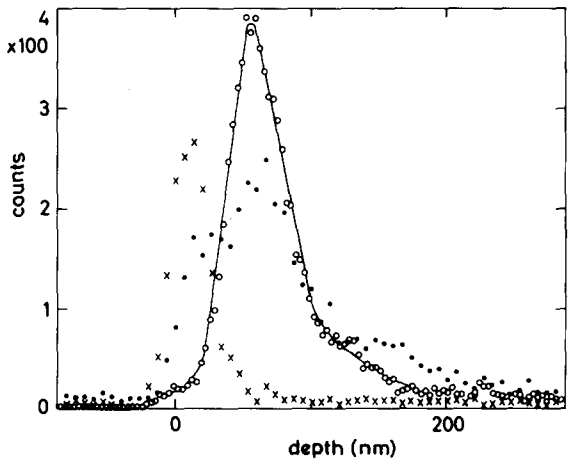

FIG. 3. Depth profile of Hf implanted in Be. The same figure shows the gettering of the oxygen by the Hf-atoms during annealing at 843 K. (a) (O) implantation energy 80 keV, (b) (×) O before annealing, (c) (O) after annealing at 843 K.

new EFG at the site of the Hf probe nuclei is caused by the trapping of oxygen at Hf.

The unique, axial symmetric EFG observed in the TDPAC experiments and the alignment of the principal component of the EFG with the *c* axis of the Be lattice can however, not be explained by an irregular arrangement of oxygen atoms in the near neighborhood of the interstitial Hf. Therefore, we suggest a configuration where a single oxygen atom is trapped in the tetrahedral cage adjacent to the one containing the Hf probe atom. Such an interstitial ⟨0001⟩ Hf-O dumbbell would explain all experimental results. In particular this model is supported by the negative sign of the EFG observed in the NO measurement. Due to its considerably larger electronegativity oxygen can be treated as negative relative to the Hf atom and for such a configuration a negative EFG is expected.

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